

(11) Publication number : 2001-172302

(43) Date of publication of application : 26.06.2001

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CLAIMS

[Claim(s)]

[Claim 1] Cellulose carbamate sponge 0.05-1, and whose bulk specific gravity the degrees of substitution are the ranges of 0.01 - 0.5 g/cm³.

[Claim 2] A manufacturing method of cellulose carbamate sponge adding and solidifying a porosity-ized agent in a cellulose carbamate solution.

[Claim 3] A manufacturing method of the cellulose carbamate sponge according to claim 2 which is at least one sort as which the above-mentioned porosity-ized agent was chosen from a salt cake, hydrous gel particles, inorganic carbonate, or a surface-active agent.

[Claim 4] A manufacturing method of a cellulose sponge adding a porosity-ized agent in a cellulose carbamate solution, and performing coagulation and reproduction simultaneously with heating.

[Claim 5] A manufacturing method of the cellulose sponge according to claim 4 which is at least one sort as which the above-mentioned porosity-ized agent was chosen from a salt cake, hydrous gel particles, or a surface-active agent.

[Claim 6] A manufacturing method of a cellulose sponge reproducing cellulose carbamate sponge obtained with a manufacturing method of a statement by claim 2 or either of 3 with an alkali solution.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to cellulose carbamate sponge and a manufacturing method for the same. It is related with the method of manufacturing a cellulose sponge, performing simultaneously the coagulation and reproduction of the cellulose carbamate solution which added the porosity-ized agent, or by reproducing cellulose carbamate sponge.

[0002]

[Description of the Prior Art] Generally the cellulose sponge is used for various materials, such as shock absorbing material including the daily-needs fields for tableware washing etc., an absorbent, microbe immobilization support, and a drugs discharge carrier.

[0003] After the above-mentioned cellulose sponge makes the viscose which dissolved cellulose ZANTOGEN acid chloride in water or alkali mix, fabricate and carry out heating coagulation of a

reinforcing fiber or the salt cake, it is manufactured by performing reproduction by acid treatment. [0004]However, toxic high carbon bisulfide is extremely used for the above-mentioned viscose at the time of preparation, and when acid treatment is carried out, the separated carbon bisulfide reacts to acid and it carries out the byproduction of the too harmful hydrogen sulfide. In order to remove the sulfur compound which remained in the cellulose sponge, it is necessary to add a desulfurization process into a manufacturing process.

[0005]On the other hand, how to carbamate-ize cellulose and to obtain sponge can be considered. The function as a cellulose sponge is exhibited by giving a carbamate group, and also demonstrating adsorption capacity and biodegradability-proof, such as outstanding metal, is expected.

[0006]

[Problem(s) to be Solved by the Invention]However, the cellulose carbamate sponge which has a carbamate group is not known until now. For example, in order to manufacture textiles or a film, the example which uses a cellulose carbamate solution is indicated for convenience by JP,61-89201,A and JP,63-36601,B. However, this is not what does not obtain sponge and used the function of the carbamate group effectively.

[0007]The cyanoethylation cellulose sponge which added and manufactured a salt cake and acrylonitrile to viscose as cellulosic sponge at JP,7-242767,A is indicated. However, since viscose is used as a raw material, it has the above-mentioned problem. This cyanoethylation cellulose sponge aims at making cellulase resistance increase, and is not what was going to use the function of the cyanoethyl group effectively.

[0008]The method of carbamate-izing regenerated cellulose material of particle state to JP,9-99238,A, and using for it as water treatment adsorbent as an invention using the function of the carbamate group, with the porosity manufactured from viscose, is proposed. However, since it becomes a solid-liquid heterogeneous reaction, it is very difficult to perform a carbamate-ized reaction uniformly. Since viscose is used as a raw material, it has the above-mentioned problem. In order to perform a carbamate-ized reaction after fabricating the porous cellulose material from viscose, it leads to the steep increase in a manufacturing process number, and is not realistic further again.

[0009]Then, this invention solves the above-mentioned problem, and handling and manufacture are safe and easy for it, and aim it at providing the cellulose carbamate sponge which has uniform porous structure, and its manufacturing method.

[0010]

[Means for Solving the Problem]This invention solves the above-mentioned technical problem, when the degree of substitution provides cellulose carbamate sponge 0.05-1, and whose bulk specific gravity are the ranges of 0.01 - 0.5 g/cm³.

[0011]The above-mentioned cellulose carbamate sponge can be manufactured by dissolving in an alkali solution, making it a cellulose carbamate solution, and adding and solidifying a porosity-ized agent to this, after carbamate-izing cellulose by urea, biuret, etc.

[0012]

[Embodiment of the Invention]Hereafter, the embodiment of this invention is described.

[0013]The degrees of substitution are [0.05-1, and the bulk specific gravity of the cellulose carbamate sponge concerning this invention] the ranges of 0.01 - 0.5 g/cm³.

[0014]The above-mentioned degree of substitution means the number of substitution of an average of the carbamate group to the 1 glucose unit in cellulose. If the degree of substitution is smaller than 0.05, neither metal adsorption capacity nor biodegradability-proof may be demonstrated enough. The hydroxyl group of the cellulose which can be replaced by a carbamate group is mainly called hydroxyl group of the 6th place, and is difficult to manufacture that in which the degree of substitution exceeds 1.

[0015]The above-mentioned bulk specific gravity means the specific gravity at the time of considering that uniform density distribution is made about the sponge which has an opening and a

stoma. If bulk specific gravity is smaller than 0.01 g/cm^3 , the mechanical strength of a Plastic solid will fall remarkably. When larger than 0.5 g/cm^3 , intensity is high, but the opening per unit capacity becomes small and the characteristics, such as pliability and absorbency, fall remarkably.

[0016]Next, the manufacturing method of the cellulose carbamate sponge which fulfills the above-mentioned conditions is explained.

[0017]First, it once dries and moisture is removed, after impregnating a urea solution with cellulose. Next, it heats more than the melting point of urea, and a cellulose carbamate is compounded by making it react. Although the degree of substitution is controllable by reaction temperature or reaction time at this time, reaction temperature is too high, or since the fall of a degree of polymerization is remarkable when reaction time is too long, a reaction condition is suitably chosen for the purpose. A cellulose carbamate can be manufactured also by the method that it is publicly known in addition to the above-mentioned method.

[0018]Subsequently, a cellulose carbamate is dissolved in an alkali solution, a cellulose carbamate solution is manufactured, and a porosity-ized agent is added and solidified in this cellulose carbamate solution. Thereby, cellulose carbamate sponge is obtained.

[0019]Especially if the above-mentioned alkali solution is a solution which has alkalinity, it will not be limited, but arbitrary solvents, such as sodium hydroxide solution and a potassium hydroxide solution, are used. As for the alkali concentration of the alkaline aqueous solution, when sodium hydroxide solution is used as an alkali solution, 5 to 12 % of the weight is preferred. If lower than 5 % of the weight, the solubility of a cellulose carbamate will become low. If higher than 12 % of the weight, viscosity will become high and mixing with a porosity-ized agent will become difficult. Since the cellulose carbamate is unstable in an alkali solution, low-temperature one of the melting temperature of the cellulose carbamate to an alkali solution is preferred.

[0020]As for the cellulose carbamate concentration in a cellulose carbamate solution, 3 to 15 % of the weight is preferred. If lower than 3 % of the weight, the mechanical strength of cellulose carbamate sponge will become low. If higher than 15 % of the weight, viscosity will become high and mixing with a porosity-ized agent will become difficult.

[0021]The above-mentioned porosity-ized agents are the drugs for porosity-izing, when solidifying a cellulose carbamate solution, and the kind and the amount of the porosity-ized agent used are suitably chosen according to physical properties, such as porous structure of cellulose carbamate sponge, and bulk specific gravity. For example, a salt cake, hydrous gel particles, inorganic carbonate, a surface-active agent, etc. are raised.

[0022]When the above-mentioned porosity-ized agent is a salt cake, the particle size is suitably chosen according to the aperture made into the purpose. As for the amount used, one to 100 times are preferred to the cellulose carbamate weight which is suitably chosen according to the bulk specific gravity made into the purpose, and is contained in a cellulose carbamate solution. The cellulose carbamate sponge which can be manufactured at this time serves as a communicating hole, when the salt cake of a porosity-ized agent is eluted.

[0023]As for the amount used, when the above-mentioned porosity-ized agents are hydrous gel particles, 0.05 to 100 times are preferred to the cellulose carbamate weight which is suitably chosen according to the bulk specific gravity made into the purpose, and is contained in a cellulose carbamate solution. As the above-mentioned hydrous gel particles, hydrous gel particles, such as agar, a carrageenan, galactoglucomannan, glucomannan, xanthan gum, gelatin, and collagen, can be raised. At this time, the cellulose carbamate sponge which can be manufactured serves as a communicating hole, when the hydrous gel particles of a porosity-ized agent dissolve and flow out.

[0024]When the above-mentioned porosity-ized agent is inorganic carbonate, the amount used is suitably chosen according to the bulk specific gravity made into the purpose, to the cellulose carbamate weight contained in a cellulose carbamate solution, there is compared with 0.5 to 5 times, and a salt cake and hydrous gel particles, and it ends. [dramatically little] However, in order to use that inorganic carbonate contacts acid, carbon dioxide is emitted and this method foams, unless it is

comparatively thin sponge, uniform porous structure is not acquired. The cellulose carbamate sponge manufactured at this time has carbon dioxide in the tendency used as the pore shape prolonged toward the surface as a byroad. Calcium carbonate, barium carbonate, etc. are raised as the above-mentioned inorganic carbonate.

[0025]When the above-mentioned porosity-ized agent is a surface-active agent, the cellulose carbamate solution which added the surface-active agent is agitated at high speed, and is whipped, and it porosity-izes by solidifying it. The amount used is suitably chosen according to the bulk specific gravity made into the purpose, to the cellulose carbamate weight contained in a cellulose carbamate solution, there is compared with an above-mentioned salt cake, hydrous gel particles, or inorganic carbonate, and below 0.1-% of the weight or more solubility ends. [further dramatically little] When less than 0.1 % of the weight, even if it generates air bubbles, since the air bubbles are unstable, there is a tendency which disappears. If the quantity beyond the solubility of the surface-active agent is added, air bubbles will be maintained stably, but since the process of elution removal of a surface-active agent is too much needed after coagulation, the addition of a surface-active agent has even a preferred dissolved amount to a cellulose carbamate solution. The structure of the cellulose carbamate sponge manufactured at this time tends to serve as a very fine independent hole.

[0026]As the above-mentioned surface-active agent, anionic detergents, such as a sulfonate and carboxylate, Ampholytic surface active agents, such as nonionic surfactants, such as cationic surfactants, such as ammonium salt, polyether, and higher alcohol, a betaine type, an amide betaine type, an imidazoline type, and an amine-oxide type, etc. can be raised.

[0027]It is more desirable to use a salt cake, hydrous gel particles, or a surface-active agent, since there is a possibility that foaming may become uneven when inorganic carbonate is used as a porosity-ized agent when obtaining the cellulose carbamate sponge of block like shape.

[0028]When intensity is required of the cellulose carbamate sponge concerning this invention, a reinforcing fiber can be added in the above-mentioned cellulose carbamate solution.

[0029]The kind of the above-mentioned reinforcing fiber is not limited unless it interferes with the mixture dispersion to a cellulose carbamate solution. For example, what it was independent or was mixed two or more kinds is raised in inorganic system textiles, such as synthetic fibers, such as semi-synthetic fibers, such as regenerated fiber, such as natural fibers, such as hemp, pulp, and cotton, rayon, and collagen, and acetate, polyester, nylon, and an acrylic, carbon fiber, and glass fiber, etc. Refining of them may be carried out by physical, chemical, and biological means.

[0030]Although the length of the above-mentioned reinforcing fiber is based also on the kind of textiles, its 0.5-30 mm is preferred. In less than 0.5 mm, the reinforcing effect by textiles does not show up easily. If it exceeds 30 mm, textiles will become entangled, and it is [become / the thing of the shape of fluff or the shape of string / easy to be made] hard to distribute uniformly.

[0031]Although the rate of the above-mentioned reinforcing fiber is based also on the solids concentration of the grade, the purpose, and cellulose carbamate solution to reinforce, it is preferred to the cellulose carbamate weight contained in a cellulose carbamate solution. [of 0.05 to twice] If it is less than 0.05 time, the reinforcing effect by textiles will not show up easily, and if twice is exceeded, it will become difficult to distribute uniformly.

[0032]Although the above-mentioned reinforcing fiber can also be added and mixed in a cellulose carbamate solution, a solid cellulose carbamate and reinforcing fiber are also simultaneously mixable with an alkali solution at the time of cellulose carbamate solution preparation.

[0033]Shaping of the cellulose carbamate solution which added the reinforcing fiber [above / porosity-ized agent and if needed] may put a sponge undiluted solution into a mold, and as long as it is thin, it may extrude it from a T die etc.

[0034]The fabricated sponge undiluted solution is solidified by a predetermined method. The methods of this coagulation involve the method by an acid solution, the method by salting in liquid, the method by an organic solvent, etc. When performing coagulation by acid, as the acid, organic acid, such as inorganic acid, such as sulfuric acid and chloride, and acetic acid, can be used. The

method of immersing the fabricated sponge undiluted solution in the above-mentioned acid as a solidifying method is raised. As for the acid concentration at this time, in the case of sulfuric acid, 0.1-5 N is preferred. When thicker [if thinner than a decinormal, coagulation will take time, and] than 5 N, in order that hydrolysis of the cellulose by acid may break out, the intensity of sponge falls remarkably.

[0035]The solidifying method with salting in liquid is the method of solidifying a sponge undiluted solution by curing salting using the thick solution of mineral salt. As the above-mentioned salt, ammonium chloride, ammonium sulfate, sodium sulfate, sodium chloride, etc. are raised, and these can be used, mixing independently or suitably.

[0036]The solidifying method by an organic solvent is the method of drying moisture from a sponge undiluted solution using an organic solvent, and solidifying a sponge undiluted solution. As the above-mentioned organic solvent, a water-soluble thing is good, and methanol, ethanol, 1-propanol, 2-propanol, etc. are raised.

[0037]It may be used combining these solidified solutions.

[0038]The solidified body of the cellulose carbamate obtained by a porosity-ized agent producing elution, fusion, foaming, etc. in the case of the above-mentioned coagulation becomes sponge-like.

[0039]The obtained cellulose carbamate sponge is processed with a bleach etc. if needed. When using a sodium hypochlorite aqueous solution as a bleach, a bleaching process may perform a sponge undiluted solution after coagulation and rinsing. Or a bleach may be added simultaneously with the alkali solution which is a solvent at the time of the cellulose carbamate dissolution. The dissolution and bleaching of a cellulose carbamate can be simultaneously performed by doing so, and a manufacturing process can be skipped.

[0040]Although any may be sufficient as the drying method of cellulose carbamate sponge, since it will contract if it dries rapidly, mild conditions are preferred.

[0041]The obtained cellulose carbamate sponge is combined with character which a cellulose sponge has, such as pliability and absorbency, and it has the adsorption capacity and the biodegradability-proof by a carbamate group.

[0042]Although the above-mentioned cellulose carbamate sponge remains as it is and can be used, it can make this a cellulose sponge.

[0043]That is, by immersing the solidified cellulose carbamate sponge in 0.1 to 10% of alkali solution, a carbamate group ****s, cellulose is reproduced and a cellulose sponge is obtained. At this time, the reproduction to cellulose advances promptly, so that immersion temperature is high. The above-mentioned alkali solution can be used as this alkali solution.

[0044]By the way, as a method of obtaining a cellulose sponge, The sponge undiluted solution which it not only reproduces the solidified above-mentioned cellulose carbamate sponge, but added the reinforcing fiber [above / porosity-ized agent and if needed] in the cellulose carbamate solution can be fabricated, and the method of performing the coagulation and reproduction of this simultaneously can be raised.

[0045]If it solidifies with heating at this time, since a carbamate group is unstable in an alkali solution, not only coagulation but reproduction will take place simultaneously.

[0046]As for the temperature at this time, 20-250 ** is preferred. If coagulation temperature is lower than 20 **, time is taken too much for a long time, and is not industrial. If higher than 250 **, the pyrolysis of a cellulose carbamate will start. Since a complete process cycle can carry out under alkali atmosphere from the dissolution of a cellulose carbamate to rinsing depending on this heating coagulation, waste of acid can be cut down. Compared with the case of viscose, since the desulfurization process is unnecessary, a manufacturing process can be simplified. As a porosity-ized agent which can be used at this time, a salt cake, hydrous gel particles, and a surface-active agent are raised.

[0047]

[Example]Next, although an example explains this invention still in detail, it is not limited only to

these examples.

[0048](Manufacture of a cellulose carbamate solution) after immersing N material dissolving pulp in urea solution 50%, by deliquoring with a centrifuge, urea of actual size was made to hold to pulp by a dry weight ratio, and it appeared in it, and dried within the homoiothermal dryer. Subsequently, after making it react at 145 °C for 12 hours, the cellulose carbamate of the degree of polymerization 400 and the degree 0.16 of substitution was obtained by making it rinse and dry.

[0049]Distribute in the water 139.5g and 14 g of this cellulose carbamate (the degree of polymerization 400, the degree 0.16 of substitution) at -5 °C. The sodium hydroxide solution 46.5g was added 36%, it agitated for 3 hours, and the cellulose carbamate solution (7% of cellulose carbamate concentration, 8.4% of alkali concentration, viscosity 12,000 mPa·s) was prepared.

[0050](Example 1) To the cellulose carbamate weight contained in the above-mentioned cellulose carbamate solution, 25 times as many salt cakes (sodium-sulfate 10 hydrate: made by Kanto Kagaku) were added, and it mixed. This was fabricated to the sheet shaped on the glass plate, and it solidified in 2N sulfuric acid solution for 1 hour. Then, it rinsed and dried and cellulose carbamate sponge was obtained. This sponge was bulk-specific-gravity 0.067g/cm^3 and the degree 0.12 of substitution. The IR spectrum of the obtained cellulose carbamate sponge is shown in drawing 1.

[0051]It has checked that it was the carbamate-ized sponge from the peak of the carbonyl group of carbamate group origin being looked at by 1715 cm^{-1} .

[0052](Example 2) Agitation mixing of the 1.5 times as much calcium carbonate (Japanese east powdering Industrial company make : NS2500) was added and carried out to the cellulose carbamate weight contained in the above-mentioned cellulose carbamate solution. This was fabricated to the sheet shaped on the glass plate, and it was made to solidify and foam with 3N hydrochloric acid aqueous solution for 100 minutes. Then, it rinsed and dried and cellulose carbamate sponge was obtained. This sponge was bulk-specific-gravity 0.15g/cm^3 and the degree 0.12 of substitution.

[0053](Example 3) To the cellulose carbamate weight contained in the above-mentioned cellulose carbamate solution, 15 times as many hydrous gelatin gel particles were added, and it mixed. This was fabricated to the sheet shaped on the glass plate, and was solidified with 2N sulfuric acid for 1 hour. Then, cellulose carbamate sponge was obtained hot-water washing and by drying. This sponge was bulk-specific-gravity 0.077g/cm^3 and the degree 0.15 of substitution.

[0054]The above-mentioned hydrous gelatin gel particles swell the dried powder end of gelatin (made by Nitta Gelatin, Inc., Inc.) with the 4 times as many water with weight in 5 °C.

[0055](Comparative example 1) Viscose for cellophane manufacture (9.5% of cellulose concentration, the ammonium chloride value 7, 5.6% of alkali concentration, viscosity 5,500 mPa·s) was diluted to 7% of cellulose concentration. To the cellulose weight contained in viscose, 60 times as many salt cakes were added, and it mixed. In 2N sulfuric acid solution, it reproduced to cellulose, and it desulfurized and bleaching-processed, and dried [this was fabricated to the sheet shaped on the glass plate, at 105 °C, it heating-solidified and ranked second for 30 minutes, and], and the cellulose sponge was obtained. This sponge was bulk-specific-gravity 0.064g/cm^3 . It was generated by hydrogen sulfide at the time of reproduction.

[0056](Adsorption test) The adsorption test of Ag^+ was done about the cellulose sponge obtained by the cellulose carbamate sponge and the comparative example 1 which were acquired in Example 1. An adsorption test in 50 ml of 4 ppm Ag^+ solution (buffer solution of Clark Lubs: pH5.8). After adding 150 mg of each sample and shaking continuously for 1 hour, the residual Ag^+ concentration of supernatant liquid was measured by the analytical curve method using the atomic absorption photometer (Shimadzu AA-6500S). As a result, by cellulose carbamate sponge, it was 12% to an Ag^+ extraction ratio being 3% in a cellulose sponge. This showed that cellulose carbamate sponge had the characteristic which excelled the cellulose sponge in the adsorption capacity of Ag^+ .

[0057](Example 4) To the above-mentioned cellulose carbamate solution 100g, a 0.2-g surface-active agent (dodecyltrimethylammonium bromide: made in Tokyo Chemicals) was added, and the

cellulose carbamate mixed liquor which contained air bubbles in large quantities by high-speed churning was obtained. This was fabricated to the sheet shaped on the glass plate, and 1-hour coagulation and reproduction of it were done at 110 °C. Then, it rinsed and the cellulose sponge was obtained. This sponge was bulk-specific-gravity 0.075g/cm³. It has checked that the degrees of substitution were 0.03 and the sponge reproduced nearly thoroughly.

[0058](Example 5) The cellulose carbamate sponge manufactured in Example 1 was reproduced with an 80 °C 1% sodium hydroxide solution for 1 hour, and the cellulose sponge was obtained. The IR spectrum of the obtained cellulose sponge is shown in drawing 2. The peak of the carbonyl group of the carbamate group origin seen by drawing 1 disappeared, and the degree of substitution has also checked 0.02 and that it was the sponge reproduced to cellulose nearly thoroughly.

[0059]

[Effect of the Invention]According to this invention, the cellulose carbamate sponge in which the stoma was distributed uniformly could be manufactured safely and easily, and, as for this cellulose carbamate sponge, high adsorptivity was shown to Ag⁺.

[0060]This cellulose carbamate sponge is available as chemical for water treatment with gestalten, such as a filter.

[0061]The cellulose sponge was able to be obtained by reproducing the cellulose carbamate solution which is cellulose carbamate sponge or its raw material.

[Translation done.]